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PROPANE-INSOLUBLE PITCH

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This invention is directed to a novel propane-insoluble pitch having propreties that make it particularly useful, for instance, as a roofing felt saturant and as a component in road paving compositions.

It is common knowledge that coal tar pitch and paving asphalts are not completely compatible, nor are roofing asphalts and coal tar pitch. A material compatible with both coal tar pitch and petroleum asphalt becomes a very desirable item, particularly in the roofing and road-paving industries. Unfortunately, however, materials known to be compatible with both coal tar pitch and petroleum asphalt have heretofore failed in one way or another to meet the required characteristics of a satisfactory roofing saturant or road-paving composition. For example, in road-paving the added component should have good adhesion to the aggregate, good drying properties, low viscosity for a given boiling range, acceptable odor, and little, if any, irritation to human skin. Also when provided as an extender in paving composition, the resulting asphalt aggregate mix should have good stock-piling characteristics, that is, should remain workable for relatively long periods of time, generally at least two months without hardening when stored in piles, possess good hardening characteristics when used to patch damaged asphalt pavements, and should be stable in service. When used as a saturant in the impregnation of felt for built-up roofs, the material should have good impregnation characteristics, low viscosity to facilitate handling, acceptable odor, and little, if any, irritation to human skin.

It has now been found that the propane-insoluble pitch of this invention possesses all of the aforementioned characteristics and is at the same time compatible with both coal tar pitches and petroleum asphalts. The combination of the aforementioned properties together with its compatibility with both coal tar pitch and petroleum asphalts makes the product especially valuable since it can be used successfully as a saturant in the roofing industry whether coal tar pitch or asphalt is preferred as a covering by the individual roofer and as an extender in the road-paving industry, particularly where coal tar pitch is used as a primer for the road followed by a final paving with asphalt.

The novel pitch of the present invention is obtained by the solvent extraction of petroleum bottoms derived from gasoline-producing catalytic cracking processes. The cracked oil is the residual oil produced as a result of the cracking of suitable mineral oil cracking feedstocks such as petroleum gas oils in the presence of catalysts such as silica-alumina or other catalysts, usually silica-based cracking catalysts, which are frequently in the fluidized state. In distillation of the cracked oil, generally at about 7 to 25 p.s.i. pressure to a maximum or end point of about 650 to 750° F., to obtain gasoline and gas oils overhead, there is produced a heavy residue or distillation bottoms containing entrained catalyst. To remove the catalyst, the residue is usually permitted to remain quiescent for a sufficient period of time to allow the catalyst particles to settle out, at which time the residue substantially free of catalyst may be decanted. In lieu of settling, the catalyst particles may be filtered or centrifuged from the oil, or such operations may be used in conjunction with settling.

In any case, there is obtained a clarified slurry oil, also referred to in the art as clarified oil. Clarified oil feeds suitable for production of the pitch of the present invention boil primarily in the range of about 400 to 1000° F. and have a 5 volume percent distillation point of at least about 500° F. or even about 600° F. and 95 volume percent distillation point of at least about 800° F. with at least 100° F. units or even at least about 200° F. units, separating the 5 percent distillation point and the 95 percent distillation point. The clarified oil feed for solvent extraction can be the full range clarified oil, that is, the entire bottoms obtained as aforementioned by the distillation of the oil from the cracking unit or it can be suitable bottoms fractions of the full range clarified oil, for example, a bottoms fraction having a 5 volume percent distillation point of below about 700° F. obtained, for instance, by vacuum distillation of the clarified oil, usually to about 50% or less bottoms. It is preferred that the cracking unit from which the clarified feed is obtained be operated at at least 50 percent conversion. Also, for reasonable yields of pitch from extraction, it is preferred that the clarified oil feed have an API of up to about 25.

The clarified oil feed is solvent extracted to provide the pitch of the invention as a raffinate or bottoms phase, an upper extract phase containing solvent and deasphalted oil also being produced. Separation of the upper phase provides the pitch of the invention, usually after any solvent in the raffinate is removed. Solvents suitable for use in the extraction are, for example, C_3 to C_5 paraffins, especially normal paraffins, with propane being preferred. Any solvent remaining in the pitch separated can be removed by simply heating at an elevated temperature generally about 300° F., for a few minutes.

The solvent to oil ratios and temperatures employed in the extraction will vary depending, for example, on the boiling range of the clarified oil feed, the solvent selected and the purpose for which the pitch product is intended, but in any event are selected to provide a pitch product having a specific gravity 77/77° F. of about 1.0500 to 1.1900; a minimum viscosity SUS at 210° F. of about 60 and a minimum needle penetration at 77° F., 100 grm./5 sec. (ASTM–D–5) of about 20. Where the pitch of the invention is to be used as a roofing saturant, for example, it is preferred to have a needle penetration at 77° F. of about 50 to 80 and a softening point of about 110 to 120° F. whereas when the pitch is to be used as a paving material it preferably should have a viscosity at 210° F. of about 60 to 80 SUS. Generally, the solvent to oil volume ratios employed in the extraction will fall in the range of at least about 2, say about 3 to 8:1 and the temperature utilized for the extraction will often range from about 130° F. to 200° F. Although a single extraction may provide the desired pitch, a number of extractions may be employed. Ordinarily the solvent extraction conditions are those which reduce the clarified oil to at least about 5% bot-

toms or raffinate, generally about 5 to 50% bottoms, based on the full range clarified oil. In cases where a select bottoms fraction of the full range clarified oil is solvent extracted, the percent bottoms, based on the select fraction may of course be greater than 50%, generally up to about 60% or more. In producing roofing saturant, for instance, the extraction is preferably conducted in a manner that provides bottoms based on the full range clarified oil of about 10 to 20%, while in the case of paving materials the bottoms are more often obtained in about 25 to 40% yield.

The pitch of the invention can be used as such either as a roofing saturant or paving material but also has the added advantage of being able to tolerate, especially in the making of paving materials, dilution with untreated clarified oil without losing mutual compatibility with asphalt and coal tar. For paving purposes, the pitch of about 50–80 penetration at 77° F., 100 g./5 sec. can be cut back with up to about 55% clarified oil.

The following examples are included to further illustrate the invention but are not to be considered limiting.

EXAMPLE I

A clarified oil having the physical properties shown in column 1 of Table I below obtained from the fluidized catalytic cracking of petroleum gas oil, was distilled by steam vacuum distillation to a 50% bottoms fraction.

The 50% bottoms fraction was then extracted with propane for six passes, using a solvent to oil ratio of 3/1 in each pass. The extractions were made by mixing the clarified oil bottoms fractions with propane in a closed batch treating kettle for 30 minutes at successive pass temperatures of 190° F., 180° F., 170° F., 160° F., 150° F., and 140° F. The mixture was permitted to settle for three hours, on each pass, until two separate phases were obtained. The deasphalted oil was drawn from the treater of each pass and additional propane added to the remaining bottoms, until after six passes the desired pitch-like material was obtained. The pitch represented 9.4% of the full range clarified oil feed (column 1). The small amount of propane contained in the pitch was then removed by heating for a few minutes at 300° F.

The pitch obtained tested as shown in Table I, column 5. Two other pitches, shown in columns 6 and 7 of Table I, were also obtained from the 50% bottoms clarified oil in a similar manner but employing, in one case (column 6), a propane/oil ratio of 5 to 1, with 7 passes, 4 at 190° F. and one each at 180°, 160° and 140° F., and in the other case (column 7), a propane/oil ratio of 7 to 1 with a single pass at 190° F. The pitch of column 6 represented 9.7% of the full range clarified oil and the pitch of column 7, 35% of the full range clarified oil. Tests on these pitches are also reported in Table I, columns 6 and 7.

Each of the clarified oil pitches was tested for compatibility with a coal tar pitch, an air blown asphalt and an asphalt obtained from vacuum distillation of crude oil. The physical properties of the coal tar pitch, air blown asphalt and vacuum distillation asphalt are shown, respectively, in columns 13, 14, 9 and 10 in Table I. For comparison the gas oil fed to the fluid unit catalytic cracker (column 2), clarified oil obtained therefrom (column 1) and residuals from vacuum distillation of the full range clarified oils to 10% and 30% bottoms (columns 3 and 4 respectively) were also similarly tested for compatibility with the asphalts and coal tar pitch. Also included are compatibility tests for the asphalts with each other and with the coal tar pitch and residues obtained by similar propane extractions of a petroleum aromatic extract (column 8) and reduced crudes (columns 11 and 12).

The compatibility test comprised blending the components 50/50 by weight at 250° F. and permitting the blends to stand in an oven at 200° F. for 2 hours. The blends were then examined visually (at 200° F.) and under the microscope (at 77° F.) for any indication of separation. The results are reported in Table I.

Table I

	Clarified Oil From Fluid Catalytic Cracking	Gas Oil Charge to Fluid Catalytic Cracking		Residue from Vacuum Distillation of Clarified Oil		Residue from Propane Extraction of Clarified Oil		
Column No.	(1)	(2)		(3)	(4)	(5)	(6)	(7)
Laboratory Tests:								
Specific Gravity at 77° F.	.9660	.9042		1.1256	1.0693	1.1848	1.1712	1.0862
Softening Point (R & B) ° F.				115		123.5	111	
Pentration at 77° F.				60		22	53	
Viscosity:								
Saybolt Universal at 210° F. (SUS)	45	45		1130	85		630	65
Saybolt Furol at 210° F.								
Color	(1)	(1)						
Compatibility of Blends With 50% Coal Tar Pitch (Col. 13):								
Visual	(2)	(2)		(4)	(4)	(3)	(3)	(3)
Under Microscope				(4)	(4)	(3)	(3)	(3)
With 50% Asphalt (Col. 14):								
Visual	(3)	(3)	(3)	(3)	(3)	(3)	(3)	(3)
Under Microscope	(3)	(3)	(3)	(3)	(3)	(3)	(3)	(3)
With 50% Asphalt (Col. 10)								
Visual	(3)	(3)	(3)	(3)	(3)	(3)	(3)	(3)
Under Microscope	(3)	(3)	(3)	(3)	(3)	(3)	(3)	(3)
With (33⅓% Coal Tar Pitch (Col. 13)):								
(33⅓% Asphalt (Col. 10))								
Visual							(3)	(3)
Under Microscope							(3)	(3)
Chemical Composition:								
Saturates				10.6			4.5	
Aromatics				23.2			19.2	
Resins				16.2			2.1	
Asphaltenes				50.0			74.2	
Distillation:								
IBP, ° F.	417							
5%, ° F.	557							
95%, ° F.	918							

Table I—Continued

	Residue of Propane Extraction of Petroleum Extract	Asphalt from Vacuum Distillation of Crude Oil		Residue from Propane Extraction of Reduced Crude		Coal Tar Pitch	Asphalt Air Blown Roofing
Column No.	(8)	(9)	(10)	(11)	(12)	(13)	(14)
Laboratory Tests:							
Specific Gravity at 77° F.	1.1120	1.0390	1.0281	1.0386	1.021	1.2106	1.0459
Softening Point (R & B) ° F.	120	125	115	124	116	127	210
Penetration at 77° F.	45	53	85	52	84	17	21
Viscosity:							
Saybolt Universal at 210° F. (SUS)	5000						
Saybolt Furol at 210° F.		1980	1325	1850	1300		4000+
Color							
Compatibility of Blends With 50% Coal Tar Pitch (Col. 13):							
Visual	(2)	(2)	(2)	(2)	(2)		(2)
Under Microscope							
With 50% Asphalt (Col. 14):							
Visual	(3)	(3)	(3)	(3)	(3)		
Under Microscope	(3)	(3)	(3)	(3)	(3)		
With 50% Asphalt (Col. 10):							
Visual	(3)	(3)		(3)	(3)		(3)
Under Microscope	(3)	(3)		(3)	(3)		(3)
With (33⅓% Coal Tar Pitch (Col. 13)):							
(33⅓% Asphalt (Col. 10)):							
Visual							28.2
Under Microscope							23.5
Chemical Composition:							
Saturates			17.3				14.9
Aromatics			25.7				33.4
Resins			33.2				
Asphaltenes			23.8				
Distillation:							
IBP							
5%							
95%							

[1] Straw.
[2] Two Phases, Sludge.
[3] Complete.
[4] Slight Oil Exudation on Surface.

EXAMPLE II

Two portions of a full range clarified oil having the same physical properties as the clarified oil of Example I were separately propane extracted under conditions that provided in one case a pitch suitable as a roof saturant (I in Table II below) and in the other a pitch suitable for use as a paving material (II in Table II below). The solvent extraction conditions and the tests in the resulting pitches are also shown in Table II.

Table II

	I	II
Charge to Propane Treater	(1)	(1)
° API Gravity of Clarified Oil	15.9	15.9
Solvent to Oil Ratio	7/1	7/1
Volume Percent on Feed to Treater	15.6	36.2
Number of Passes	8	4
Temp. of Successive Passes	(2)	(3)
Tests on Pitch:		
Specific Gravity at 77° F.	1.1761	1.0858
Softening Point (R & B) ° F.	113	
Penetration at 77° F.	50	
Viscosity SUS at 210° F.	695	67

[1] Full range clarified oil.
[2] 4 at 190° F., and 1 each at 180° F., 170° F., 60° F., 140° F.
[3] 4 at 190° F.

The pitches obtained were tested for compatibility as in Example I with the coal tar pitch of column 13 in Table I above and the asphalts of columns 10 and 14 of the same table. The results of the compatibility tests are as follows.

Compatibility of Blends	(1)	(2)
With coal tar pitch (col. 13) visual and under microscope	Complete	Complete.
With asphalt (col. 14) visual and under microscope	do	Do.
With asphalt (col. 10) visual and under microscope	do	Do.

The following example demonstrates the use of the pitch of the invention as a satisfactory saturant for roofing felt with either conventional roofing pitch or asphalt.

EXAMPLE III

The pitch-like material of column 6, Table I was used to saturate a paper roofing felt. The weight of pitch-like material used as saturant was 160% based on dry paper. Weatherometer tests were run to compare the felt saturated with the pitch-like material with felts commercially saturated with coal tar and with asphalt saturants. Test specimens were prepared as follows. 2¼" x 5" pieces of three felts were placed on galvanized steel plates with a 1/16" high retaining rim around the edges and were each covered with a 0.025" thick layer of roofing asphalt. Separate similar specimens were also prepared using roofing pitch. These six specimens were subjected to 30 weatherometer cycles, consisting of 16 hours exposure to a carbon arc light at 130° F. ambient temperature, 1 hour soaking time in water at 77° F. and 7 hours drying in air at 77° F.

The appearance of the samples after 30 weatherometer cycles, given below, showed that the felt saturated with the pitch-like material of this invention performed satisfactorily with either asphalt or pitch roofing, and as well as asphalt-saturated felt with asphalt roofing or tar-saturated felt with pitch roofing. The results are summarized below:

Type of Sample	Appearance of Specimens After 30 Weatherometer Cycles
Felt saturated with tar covered with pitch roofing.	Surface glossy and smooth.
Felt saturated with tar covered with asphalt roofing.	Surface dull and blistered.
Felt saturated with asphalt covered with pitch roofing.	Surface dull, cracked and blistered.
Felt saturated with asphalt covered with asphalt roofing.	Surface glossy and smooth.
Felt saturated with pitch-like material of this invention covered with pitch roofing.	Do.
Felt saturated with pitch-like material of this invention covered with asphalt roofing.	Do.

The following example demonstrates use of the pitch material of the present invention in making an excellent winter stockpile paving mix.

EXAMPLE IV

A paving mix having the following composition was made.

Composition of mix:	Weight percent
Sand and limestone mix*	92.5
85–100 penetration paving asphalt	5.0
Pitch-like material of this invention (column 7, Table I)	2.5

*Sieve analysis of sand and limestone mix—

Sieve size:	Percent passing
½''	100
¾''	75
⅜''	54
No. 8	43
No. 14	32
No. 25	20
No. 52	14
No. 100	10
No. 200	7

The above mix was prepared by thoroughly drying the aggregate (24 hours at 375° F.), then mixing the aggregate asphalt and pitch-like material at 300–325° F. for 1 minute.

The resulting mix when poured out in a pile was easily handled and could be scooped readily at 77° F. This mix when in a pile remained workable for three months, but when placed as a patch in a hole about 1 foot in diameter and 1'' deep in a damaged asphalt pavement, provided a stable patch immediately after compacting. This patch hardened noticeably in one week. Difficulties with other stockpile mixes are that they harden in the stockpile, are not stable in service, or do not harden after patch application.

It is claimed:

1. A propane-insoluble pitch having a specific gravity, 77/77° F., of about 1.0500 to 1.1900, a minimum viscosity SUS at 210° F. of about 60, and a minimum needle penetration at 77° F., 100 gms./5 sec. of about 20, prepared by solvent extracting a petroleum bottoms feedstock produced from the catalytic cracking of petroleum gas oil, said feedstock boiling primarily in the range of about 400 to 1000° F. and having a 5 volume percent distillation point of at least about 500° F. and a 95 volume percent distillation point of at least about 800° F. with at least about 100° F. units separating the 5 volume percent distillation point and 95 volume percent distillation point, said solvent extracting being with a C_3 to C_5 paraffinic solvent at a solvent-to-oil ratio of at least about 2 to 1 and a temperature of about 130 to 200° F. to provide an extract phase and a raffinate phase and separating the phases to provide said pitch.

2. The pitch of claim 1 wherein the paraffinic solvent is propane and the solvent-to-oil ratio is about 3 to 8:1.

3. The pitch of claim 1 wherein the petroleum bottoms feedstock has a 5 volume percent distillation point of below about 700° F.

4. The propane-insoluble pitch of claim 1 having a viscosity of about 60 to 80 SUS at 210° F.

5. The propane-insoluble pitch of claim 1 having a needle penetration at 77° F. of about 50 to 80 and a softening point of about 110 to 120° F.

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